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Hydrodesulfurization of Crude Oil Over Co-Mo Catalysts in a Slurry Reactor

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***Abstract*—In this paper, hydrodesulfurization (HDS) of crude oil in the three-phase slurry reactor over cobalt – molybdenum catalyst (CoMo / ɣ-AL_2O_3) is studied. Effects of space velocity and length of reactor on the conversion rate and catalyst effectiveness for HDS process have been investigated. Kinetics of the reaction rate for this process is primarily and Arrhenius equation for the rate constant is used. The results show that the effectiveness factor for catalyst along the length of reactor is decreased about 83%.**

By increasing liquid velocity from 4 to 10 1/s, the conversion of sulfur components is decreased about 22% at the temperature of 523 K. At the same temperature, by increasing liquid velocity from 36 to 84 1/s conversion is reduced to 25%. The results of the variation of the dimensionless reaction rate against conversion show that with increasing conversion, the reaction rate decreases and the reaction is stopped when the conversion is 100%.

Keywords—Crude oil; Hydrodesulfurization; Co - Mo catalyst; Slurry reactor

I. Introduction

The process of hydrodesulfurization (HDS) is now widely used in petroleum industry. HDS is a catalytic process where the sulfur compounds in crude oil are converted to sulfur-free materials. The increasing demand for the removal of sulfur has caused much attention to this type of process. There are several studied available in literature which focused on effect of types of reactors and catalyst in HDS process [1]. Slurry reactors are used in many processes such as HDS. In these types of reactors, gas is dispersed into a pool of liquid and catalyst particles are suspended in liquid phase which provide a large interfacial area between the phases. They have many advantages such as simple design, good temperature distribution, addition and removal of the catalyst without stopping the operation and high rate of mass transfer between phases with minimal energy. HDS with metal catalyst as a complete process widely used in the world because metal catalyst has little effect substrate and it is suitable for removing sulfur compounds. The catalysts used in HDS are materials with high surface area, contains an active ingredient and an accelerator that are distributed on a base and main catalysts are those of cobalt–molybdenum and nickel–molybdenum supported on alumina that both of them can remove sulfur components [2]. Alumina has outstanding textural and mechanical properties and it is relatively cost-effective. The support is used principally to achieve better catalyst dispersion, which consequently increases the catalytic performance [3]. Cobalt-molybdenum catalyst has a low amount of hydrogenation activity and consequently if has low consumption of hydrogen for sulfur removal. Catalysts for slurry bed are unsupported and in the early times, heterogeneous solid powder catalysts such as red mud and natural ore were widely used. In order to improve the conversion, homogeneous dispersed catalysts with high catalytic activity and good performance were developed [4]. Crude oil contains sulfur, nitrogen, oxygen, metals and other unsaturated cyclic compounds that cause¬ environmental hazards, decreases the life of machinery, soil pollution, corrosion and catalyst deactivation [5].

Stricter environmental regulations have been enacted to reduce the sulfur content. Sulfur compounds in crude oil contains: free elemental sulfur, mercaptans and thiols (R-SH), H_2S, sulphides and disulfide (R-S-S-R') such as dimethyle disulfid (CH_3-S-S-CH_3), diethyl disulfide (CH_3-CH_2 -S-S-CH_2-CH_3), polysulfides (R-S_n-R') and thiophenes and their derivatives which are in heavier compounds and have high boiling point also are undesired sulfur compounds [6]. Sulfur content of crude oil is between 0.25 to 7.8 wt%, which depends on the type of source. However, for the environmental reasons, the maximum allowable content must not be more than 0.3% [7]. Desulphurisation of compounds with thiophene and dibenziothiophene is more difficult than sulfides, poly-sulphides and mercaptans. Therefore, to determine the optimal process conditions for desulfurisation by hydrogen this should include desulfurisation of thiophene compounds and their derivatives [8]. Reactions to the general case of HDS process is as follows [9]:

$$Organic\ sulfur\ compound + H_2 \rightarrow$$
$$H_2S\ + desulfurized\ organic\ compound$$

Sulfur compounds in the presence of catalyst react with hydrogen and converted to hydrocarbons and hydrogen sulfide [10]. Hydrogen sulfide obtained is in the gas phase and it can be easily removed.

Generally, the amount of sulfur in crude oil increases in the following order [11]:

$$Asphaltenes > Resins > Aromatics > Saturates$$

The most common catalyst that used in the refining with hydrogen, include oxides or sulfides of metals such as CO, Ni,,Fe Mo and all are based on alumina [12,13]. Addition of neutralized particles to the catalyst enhance catalyst wetting coefficient and thus increase work efficiency [12,14]. Two factors are used to determine the kinetics of HDS reaction: firstly compounds of sulfur should be reacted with hydrogen and the second solvent that sulfur components is scattered in this solvent and in totally are entered as a HDS liquid feed into the reactor.

The aim of the present work was to investigate desulurization of crude oil by hydrogenation using cobalt-molybdenum catalyst in a slurry reactor. Mathematical modeling for the removal of sulfur compounds in crude oil is carried out [9,15] and model is validated by the available data in literature[16,17,18,]. A simple reaction was chosen to study model,

II. Mathematical modeling

The system considers two phases: the gas phase which is mainly hydrogen and slurry phase that is composed of liquid and catalyst particles. Mass balance is shown in Eq.1 [19]:

$$\frac{\partial}{\partial \mathrm{z}}\left(D\frac{\partial(\rho_\omega\varepsilon_\omega)}{\partial z}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(Dr\frac{\partial(\rho_\omega\varepsilon_\omega)}{\partial r}\right)-\frac{\partial(u_{zw}\rho_\omega\varepsilon_\omega)}{\partial z}-\frac{1}{r}\frac{\partial(ru_{rw}\rho_\omega\varepsilon_\omega)}{\partial r}+k_1a_b\left(C_{H_{2.G}}-C_{H_{2.L}}\right)=0 \tag{1}$$

III. The catalytic effectiveness for the hydrodesulfurization

The catalysts contains macropores and micropores randomly distributed and diffusion coefficient is calculated by the following equation [20] :

$$D_e=\frac{D_{mol}}{\tau}\left\{\varepsilon_M\left[1-\left(\frac{r_{mol}}{r_M}\right)\right]^4+\varepsilon_m\left[1-\left(\frac{r_{mol}}{r_m}\right)\right]^4\right\} \tag{2}$$

IV. Mass balance for the catalyst particles:

Mass balance for the catalyst particle is obtained by the following equation [21]:

$$\frac{d\left(D_e\left(\frac{dc}{dx}\right)\right)}{dx}2\left[\frac{\varepsilon_M}{r_M}+\frac{\varepsilon_m}{r_m}\right]g(C_M) \tag{3}$$

Dimensionless equations were obtained using the following parameters:

$$u=\frac{C_M}{C_{M0}} \tag{4}$$

$$\xi=\frac{x}{L} \tag{5}$$

$$a=\frac{\varepsilon_M^0}{\varepsilon_m^0} \tag{6}$$

$$f=\frac{r_m}{r_m^0} \tag{7}$$

$$p=(1-b)^4 \tag{8}$$

$$h(u)=\frac{g(C_M)}{g(C_{M0})} \tag{9}$$

$$b=\frac{r_{mol}}{r_m^0} \tag{10}$$

$$\theta=\frac{g(c_{m0})t}{r_m^0p_d} \tag{11}$$

$$\varphi^2=\frac{2g(c_{m0})\tau L^2}{(a+p)c_{m0}r_m^0D_{mol}} \tag{12}$$

Macropores particle radius stay practically unchanged $\left(\frac{r_M}{r_M^0}\approx 1\right)$. The occupied area of the macropores is much smaller than the particle micropores ,$\left(\frac{\varepsilon_M}{r_M}\ll\frac{\varepsilon_m}{r_m}\right)$. Radius of macropores particle is much larger than the micropores particle ($r_m^0\ll r_M^0$) and the macroporosity remains practically unchanged $\varepsilon_M\approx\varepsilon_M^0$.

According to the mass conservation:

$$\frac{d}{d\xi}\left[\frac{a+f^2\left(1-\frac{b}{f}\right)^4}{a+p}\frac{du}{d\xi}\right]=\varphi^2fh \tag{13}$$

$$df/d\theta=-h \tag{14}$$

$$\eta=\frac{\left(1\middle|A_{ip}^0\right)\int g(c_m)dA_{ip}}{g(c_{m0})}=\frac{\left(1\middle|2\pi r_m^0L\right)\int g(c_m)2\pi r_mLd\xi}{g(c_{m0})}=\int_0^1\frac{r_mg(c_m)}{r_m^0g(c_{m0})}\,d\xi=\int_0^1fu\,d\xi \tag{15}$$

$$u(\xi,\theta)=\sum_{i=0}^{\infty}\theta^iu_i(\xi) \tag{16}$$

$$\frac{df}{d\theta}=-u_0(\xi)-\theta u_1(\xi) \tag{17}$$

Boundary conditions of Equation 17 is

$$f(\theta=1)=1 \tag{18}$$

$$\frac{d}{d\xi}\left[\frac{du_{0(\xi)}}{d\xi}\right]=\varphi^2u_0(\xi) \tag{19}$$

Initial conditions for Equation 19 is:

$$\frac{du_{0(\xi)}}{d\xi}\Big|_{\xi=0}=0 \tag{20}$$

$$u_0(1)=1 \tag{21}$$

$$\frac{d^2u_1(\xi)}{d\xi^2}-\varphi^2u_1(\xi)=q\frac{d^2(u_0^2)}{d\xi^2}-\varphi^2u_0^2 \tag{22}$$

$$q=\frac{(1+b)(1-b)^3}{a+p} \tag{23}$$

Boundary conditions for equation of 22 is:

$$\frac{du}{d\xi}\Big|_{\xi=0}=0 \tag{24}$$

$$u(\xi=1)=1 \tag{25}$$

$$\eta=\frac{\left(\frac{1}{2\pi r_m^0L\int g(c_s)}\right)2\pi r_mLd\xi}{g(c_{s0})}=\int_0^1\frac{r_mg(c_s)}{r_m^0g(c_{s0})}d\xi=\int_0^1fvd\xi \tag{26}$$

When the f function is obtained, it is necessary to obtain the dimensionless concentration to estimate the diffusion coefficient of HDS catalyst.

According to the mass conservation for the catalyst:

$$\frac{d}{d\xi}\left[\frac{a+f^2\left(1-\frac{b_s}{f}\right)^4}{a+p_s}\frac{dv}{d\xi}\right] = \varphi_s^2\, f\, v \tag{27}$$

$$v = \frac{c_s}{c_{s0}} \tag{28}$$

$$b = \frac{r_{mol,s}}{r_m^0} \tag{29}$$

$$\varphi^2 = \frac{2g(c_s)\tau l^2}{(a+p_s)c_{s0}r_m^0 D_{mol,s}} \tag{30}$$

$$p_s = (1-b_s)^4 \tag{31}$$

Using the theory of perturbation for $v(\xi)$:

$$v(\xi,\theta) = \sum_{i=0}^{\infty}\theta^i v_i(\xi) \tag{32}$$

$$\frac{d}{d\xi}\left[\frac{dv_0(\xi)}{d\xi}\right] = \varphi_s^2 v_0(\xi) \tag{33}$$

Boundary conditions for this case is:

$$\frac{dv_0(\xi)}{d\xi}\Big|_{\xi=0} = 0 \tag{34}$$

$$v_0(1) = 0 \tag{35}$$

According to the $f(\theta,\xi)$ function and for mass conservation of catalyst and θ ≅ 0 assumption:

$$\frac{d^2v_1(\xi)}{d^2\xi} - \varphi_s^2 v_1(\xi) = q_1\left[\frac{du_0(\xi)}{d\xi}\frac{dv_0(\xi)}{d\xi} + \frac{d^2v_0(\xi)}{d^2\xi}u_0(\xi)\right] - \varphi_s^2 u_0(\xi)v_0(\xi) \tag{36}$$

Solving the above equations are given with the following boundary conditions:

$$\frac{dv(\xi)}{d\xi}\Big|_{\xi=0} = 0 \tag{37}$$

$$v(\xi=1) = 1 \tag{38}$$

It is assumed that the reactor operates under steady state and isothermal conditions when the phase change for the light cuts is negligible.

V. The kinetic model

The reaction of HDS is considered as the first order as showed below:

$$Rate = kC_s \tag{39}$$

where k is kinetic parameter that is defined by the following equation:

$$k_{HDS} = k_0 \exp\left(-\frac{E}{RT}\right) \tag{40}$$

To calculate the kinetic constant of the reaction, Arrhenius equation is used where k_0 is Arrhenius constant, E is activation energy (kJ/mol), T is temperature (k) and R is universal gas constant (kJ/mol.k). Parameters of Arrhenius equation that are determined which include activation energy and Arrhenius constant. Therefore, HDS reaction is conducted in temperature between 523-583 K and LHSV=0.5.

VI. Results and Discussion

The results of analysis and calculations to obtain Arrhenius parameters are summarized in Table 1. Figure 1 shows the plot of ln (k) versus 1/T. Arrhenius constant and activation energy are obtained from the slope which equal to the ratio E/R and from the intercept which equal to ln(k_0). The calculated values for the activation energy and Arrhenius constant are 25.731kJ/mol and 590.458, respectively. The values are within the range for values of hydrodesulfurizatthat were reported in literature [22].

The activation energy for the reaction in the various studies is different. This may be caused by the difference between the type of catalyst used, the type of feed sulfur reference materials, reaction mechanism and the physical phenomenon of interfacial phases [23,24,25]. The data in Table 2 are used to solve the equations.

Figure 2 shows the profile of the concentration of sulfur in the reactor. As expected, by increasing the length of the reactor, the concentration of sulfur compounds is reduced. That is an indication of progress in HDS process. Comparison between the results of similar studies of modeling and experimental data with this study suggest that the work is performed carefully and indicates that the model can predict the operation of this type of reactor used in HDS process.

Figures 3 and 4 show the effects of relative liquid velocity on the conversion of sulfur in the reactor. From these figures, it can be inferred that by increasing space velocity of liquid, conversion of sulfur compounds are reduced. The reason can be attributed to the reduced time for molecules feed to penetrate the pores and active sites of the catalyst and the interaction with the site.

Figure 5 shows the effect of catalyst on the impact factor for HDM and HDS processes which represents a reduction of two compared factor of catalytic effect versus time. This is because the sulfur sitting on the metal active sites and closing them.

Figure 9 shows the conversion rate versus dimensionless reaction rate which is a straight line with a negative slope. In another words, by increasing the conversion, the reaction rate is reduced. Figure 10 shows that metalloid compounds present in the feed rate is reduced by increasing the length of the reactor.

VII. Conclusion

The reaction of cobalt-molybdenum hydrodesulfurization of crude oil using catalysts was investigated in a slurry reactor and various parameters including the substrate and temperature were investigated. Since different sulfur reactions occurred at the same time, it is feasible to consider a model in which the reaction rate appears to vary as a function of conversion. The matlab software provides the ability to conduct small-scale reactor for various operating conditions and geometric measure and the predict the operating parameters which is an important tool in the design of HDS. In summary, the focus in earlier studies were type, size and shape of the catalysts, the reactors type, kinetics that are used, process operating conditions and material contains sulfur [24,25,26]. The advantages of this study are that the chosen reactor is the best place for contact between the phases and also the catalysts have maximum efficiency and highest activity for removal of sulfur. Another advantage of this research is that the dimensionless equations are used, in addition to these and unlike similar studies both dimension is considered. The model was validated with presented data. The model satisfactorily predicted the effects of operating conditions such as temperature, space velocity and length of reactor. It is expected that information from this simple catalytic reaction model has applicability to the design and optimal operation of hydrodeulfurization.

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Table 1: Results of Arrhenius parameters C_f = 12000 ppm

Table 2- The values of variables

Nomenclature:

Figure 1- Plot of ln (k) versus. 1/T to obtain Arrhenius parameters

Figure 2- Profile of sulfur concentration along the length of the reactor

Figure 3- Effect of space velocity on the conversion at temperature of 523.15 K and the initial concentration of Cs0 = 0.5

Figure 4- Effect of space velocity on the conversion at temperature of 593.15 K and the initial concentration Cs0= 0.5

Figure 5- Effectiveness factor of catalyst for HDS and HDM processes

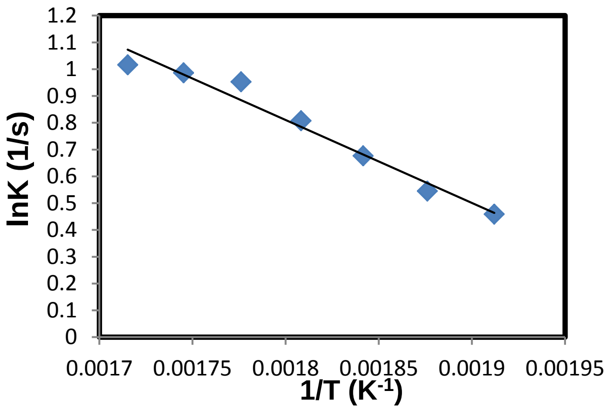
Figure 6- Comparison of this model with the work of other modeling [6]

Figure 7-Profile of sulfur concentration along radius of the reactor

Figure 8- Profile of one-dimensional and versus dimensional

Figure 9- Profile of dimensionless rate versus conversion

Figure 10- Profile of organometallic concentration versus the length of the reactor



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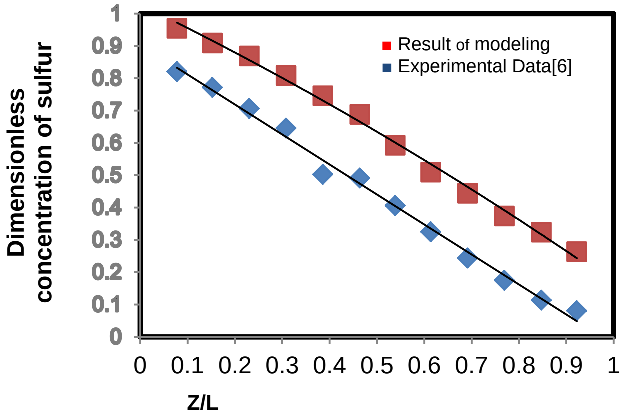


Figure 2- Profile of sulfur concentration along the length of the reactor

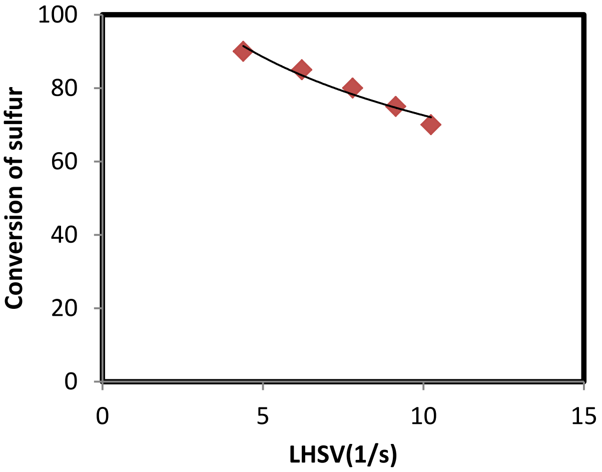


Figure 3- Effect of space velocity on the conversion at temperature of 523.15 K and the initial concentration of Cs0 = 0.5

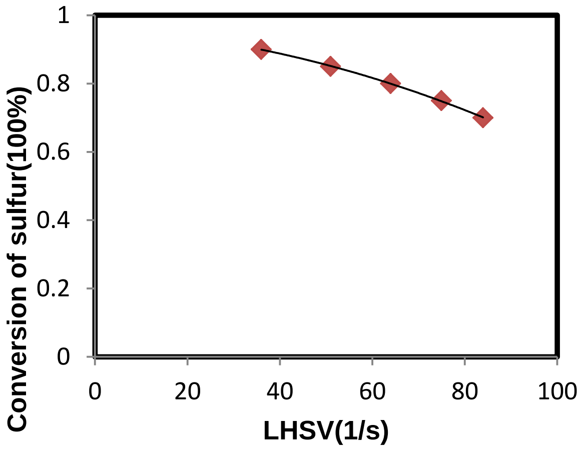


Figure 4- Effect of space velocity on the conversion at temperature of 593.15 K and the initial concentration Cs0= 0.5

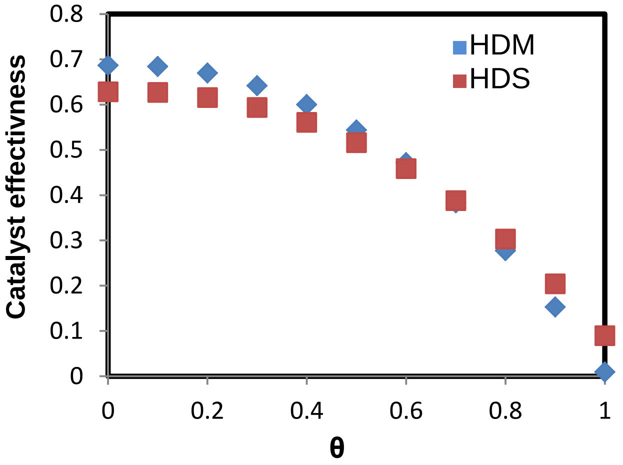
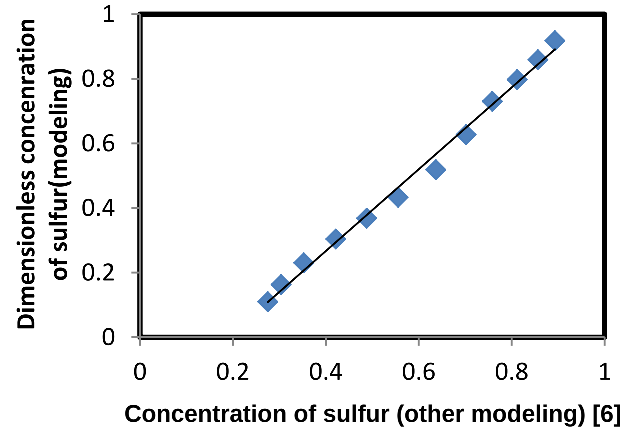


Figure 5- Effectiveness factor of catalyst for HDS and HDM processes



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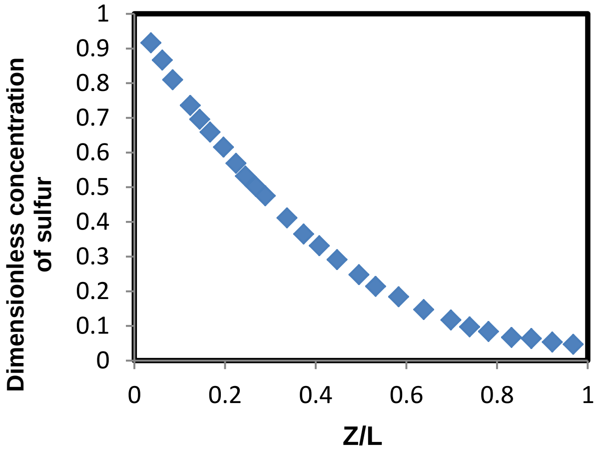

Figure 7-Profile of sulfur concentration along radius of the reactor

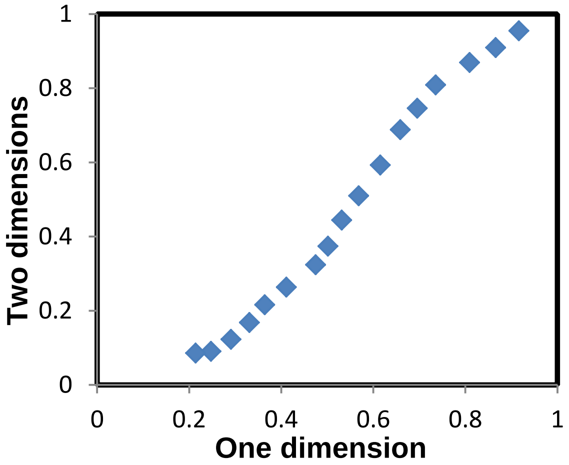

Figure 8- Profile of one-dimensional and versus dimensional

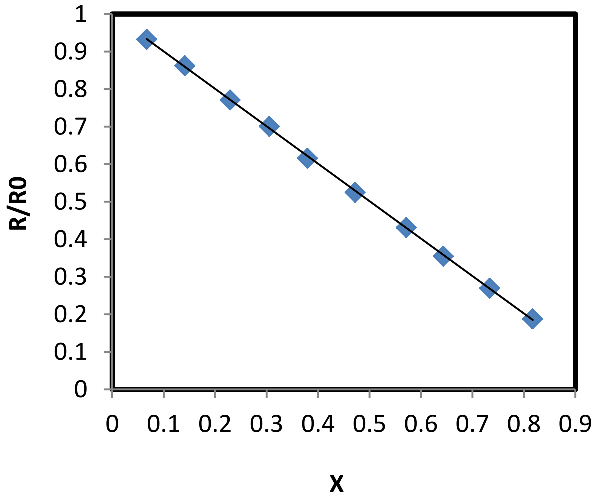

Figure 9- Profile of dimensionless rate versus conversion

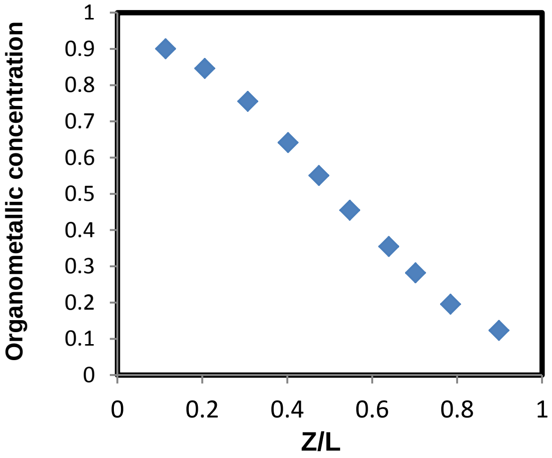

Figure 10- Profile of organometallic concentration versus the length of the reactor

Results of Arrhenius parameters :Table 1
ppm 12000 = $_f$C

(T(K	($^{1-}$LHSV(h	(ppm) $_p$C
523	0.5	423
533	0.5	318
543	0.5	196
553	0.5	113
563	0.5	56
573	0.5	47
583	0.5	40

Table 2- The values of parameters

Variable	Dimension	Value
K_{HDM}	1/s	0.41
K_{HDS}	1/s	0.29
M_0	%	1
S_0	%	1
q	-	0.9
ϕ_s	-	0.25
ϕ_2	-	2
q_1	-	1.9
ρ_{bulk}	kg_{cat}/m^3	5
$k_l a_{sc}$	1/s	1